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## VAPOR PRESSURES AND PREDICTED PARTICLE/GAS DISTRIBUTIONS OF POLYCHLORINATED BIPHENYL CONGENERS AS FUNCTIONS OF TEMPERATURE AND ORTHO-CHLORINE SUBSTITUTION

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**Abstract**—Parameters are given for calculating saturation liquid-phase vapor pressures ( $p_i^L$ , Pa) of 180 polychlorinated biphenyl (PCB) congeners as functions of temperature and ortho-chlorine substitution. These are slopes ( $m_i$ ) and intercepts ( $b_i$ ) of the equation

$$\log p_i^L = m_i/T + b_i.$$

Values of  $m_i$  and  $b_i$  were obtained from gas chromatographic retention data for 32 PCB congeners. These slopes varied regularly with homolog (number of total chlorines) and also with the number of ortho-chlorines. From this information,  $m_i$  and  $b_i$  values were estimated for 148 other PCBs whose vapor pressures had been reported at only a fixed temperature. Vapor pressure data were applied to predicting the adsorption of PCBs to aerosols at 10 and 25°C, using the Junge-Pankow equation. Particulate percentages increased with homolog number, from 2–5% for trichlorobiphenyls to >90% for octachlorobiphenyls at 10°C. Within each homolog, PCBs with fewer ortho-chlorines (and consequently lower  $p_i^L$ ) had increased particulate percentages. These results suggest that the more highly toxic mono- and non-ortho-PCBs are associated to a greater degree with particles in ambient air, and consequently more likely to be removed by precipitation and dry deposition.

**Key word index:** Semivolatile organic compounds, organochlorine compounds, vapor pressure, coplanar PCBs, particle/gas distribution.

### 1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants present as complex mixtures of the 209 possible congeners (Schulz *et al.*, 1989). Of all the congeners, a few have unusually high mammalian toxicity. PCBs having none or one chlorine in the 2 or 6 position of the phenyl ring and one or more meta- and para-chlorines on each ring can adopt a configuration in which both rings lie approximately in the same plane. In this configuration, they are sterically similar to the polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) and are potent inducers of liver microsomal aryl hydrocarbon hydroxylase (AHH) (Huckins *et al.*, 1988; Safe, 1990; Tanabe *et al.*, 1987). These so-called "coplanar" PCB congeners are usually found in much higher concentrations than PCDDs/PCDFs, and their presence in the environment has recently become a toxicological concern.

PCBs exist in air as vapors and associated with suspended particles. Adsorption to aerosols depends on the vapor pressure of the compound, the amount and type of particulate matter present, and the ambient temperature (Cotham and Bidleman, 1992; Pankow, 1987). Mono- and non-ortho-PCBs have lower vapor pressures than other congeners within the

same homolog (Bidleman, 1984). Thus they may be preferentially adsorbed to atmospheric particles, thereby increasing their chances for deposition.

To predict the degree of association of PCBs with particles, it is necessary to know the saturation liquid-phase vapor pressure ( $p_i^L$ , Pa) of each congener as a function of temperature. Vapor pressures have been determined for a large number of PCB congeners, but only at a single temperature (Foreman and Bidleman, 1985; Fischer *et al.*, 1992; Murphy *et al.*, 1987). In this work parameters for calculating the temperature dependence of  $p_i^L$  for 32 PCB congeners were derived from previously obtained gas chromatographic data (Bidleman, 1984; Hinckley *et al.*, 1990). This information was used to estimate the temperature dependence of an additional 148 PCBs as functions of homolog and number of ortho-chlorines. Vapor pressure data were then used to predict aerosol-bound fractions of PCB congeners.

### 2. VAPOR PRESSURE DETERMINATIONS

Measurement of vapor pressure by a conventional method such as gas saturation is extremely tedious, and has been done for only a few of the 209 PCB congeners. For this reason a capillary GC method was

developed to determine vapor pressures of PCBs and other non-polar compounds (Bidleman, 1984; Hinckley *et al.*, 1990). The method is based on the simple concept that partitioning of a solute between the gas and stationary phases is controlled mainly by vapor pressure. In practice, a series of isothermal runs is made at column temperatures ranging from about 70 to 120°C and the relative retention time (RRT) of the test compound to a standard is measured at each temperature. The test compound vapor pressure is determined from changes in the RRT with temperature and the known vapor pressure of the standard. Suitable standards are octadecane, eicosane, and *p*, *p'*-DDT.

Initial estimates of vapor pressure by GC were correlated to  $p_L^0$  for 19 to 24 compounds (Bidleman, 1984; Hinckley *et al.*, 1990). These were substances for which vapor pressures have been determined by gas saturation or other techniques, and included 5–7 PCB congeners as well as organochlorine pesticides and polycyclic aromatic hydrocarbons. The resulting correlations allowed  $p_L^0$  to be calculated from GC data for compounds with unknown vapor pressures. In the case of PCBs, the method was applied to the determination of  $p_L^0$  for 30 congeners at 25°C only

(Bidleman, 1984). These ranged from monochloro- to heptachlorobiphenyls, and included PCBs having different numbers of ortho-substituted chlorines. It was noted that, within each homolog,  $p_L^0$  values were lower for those congeners having fewer ortho-chlorines.

The capillary GC method also determines  $Q_1/Q_2$ , the ratio of the heats of vaporization of test (1) and standard (2) substances. Knowing  $Q_2$  allows  $Q_1$ , and thus the temperature dependence of test compound vapor pressures, to be calculated. This was done for four PCBs and several pesticides by Hinckley *et al.* (1990), using eicosane and *p*, *p'*-DDT as standards ( $Q_2 = 93.4$  and  $88.9$  kJ mol<sup>-1</sup>, respectively; Hinckley *et al.*, 1990; MacKnick and Prausnitz, 1979).

As a necessary step in calculating capillary GC-determined vapor pressures, values of  $Q_1/Q_2$  were obtained for 30 PCBs using octadecane ( $Q_2 = 84.5$  kJ mol<sup>-1</sup>) or eicosane ( $Q_2 = 93.4$  kJ mol<sup>-1</sup>) standards (Bidleman, 1984), but most of these were not reported in the 1984 paper. In this work  $Q_1$  was calculated from the 1984  $Q_1/Q_2$  data, and slopes ( $m_L = -Q_1/2.303R$ ) and intercepts ( $b_L$ ) were generated for the equation

$$\log p_L^0 = m_L/T + b_L \quad (1)$$

These parameters for 32 PCBs are listed in Table 1.

Table 1. Parameters of equation (1) for calculation of vapor pressure (Pa) for PCBs, determined by capillary GC

Con- gener *	Total chlorines	Ortho-chlorines	$m_L$	$b_L$
1	1	1	-3366	11.57
2	1	0	-3476	11.65
3	1	0	-3488	11.67
7	2	1	-3841	12.15
9	2	1	-3862	12.22
11	2	0	-3936	12.14
15	2	0	-3971	12.18
29	3	1	-4007	12.09
30	3	2	-3886	12.02
31	3	1	-4058	12.15
40	4	2	-4271	12.32
52	4	2	-4220	12.36
53	4	3	-4114	12.24
66	4	1	-4349	12.38
70	4	1	-4431	12.60
77	4	0	-4552	12.61
87	5	2	-4562	12.66
99	5	2	-4533	12.68
101	5	2	-4514	12.67
105	5	1	-4758	12.90
118	5	1	-4664	12.72
128	6	2	-4881	12.91
138	6	2	-4800	12.81
149	6	3	-4689	12.78
153	6	2	-4775	12.85
156	6	1	-4949	12.94
170	7	2	-5139	13.17
171	7	3	-5008	13.07
180	7	2	-5042	13.03
187	7	3	-4911	12.96
202	8	4	-4851	12.99
209	10	4	-5402	13.27

\*IUPAC designation.

Examination of the equation reveals that the absolute vapor pressure of a homolog. Moreover, within a homolog, vapor pressures with fewer ortho-substituted chlorines and greater slopes. When  $m_L$  is plotted against the number of ortho-chlorine groups yield a linear relationship (Fig. 1), regression of  $m_L$  vs. number of ortho-chlorine groups yield a linear relationship. These are the fitted parameters.

Foreman and Bidleman (1984) determined vapor pressures at a single temperature for 133 PCB congeners by correlating  $p_L^0$  with  $m_L$  at 200°C (OV-101 column). Bidleman (1984), Fischer *et al.* (1984) and Bidleman (1984) determined vapor pressures for 133 PCB congeners by a similar method. In this work,  $m_L$  (methyl-50% *n*-octylpolysiloxane) and reference vapor pressures for 32 PCB congeners were taken

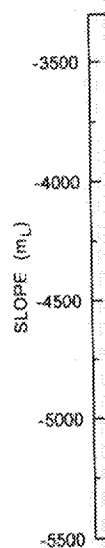


Fig. 1. Slope ( $m_L$ ) vs. Homolog.

Homolog

1  
2  
3  
4  
5  
6  
7  
8  
9  
10

\*From

ed from monochloro- to  
cluded PCBs having di-  
stituted chlorines. It was  
og,  $p_L^o$  values were lower  
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also determines  $Q_1/Q_2$ ,  
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ited. This was done for  
ides by Hinckley *et al.*  
-DDT as standards ( $Q_2$   
ectively; Hinckley *et al.*,  
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culating capillary GC-  
values of  $Q_1/Q_2$  were  
octadecane ( $Q_2 = 84.5$   
4 kJ mol<sup>-1</sup>) standards  
these were not reported  
 $Q_1$  was calculated from  
es ( $m_L = -Q_1/2.303R$ )  
ated for the equation

$$+ b_L. \quad (1)$$

are listed in Table 1.

Examination of the equation (1) slopes for these PCBs reveals that the absolute values of  $m_L$  increase with homolog. Moreover, within a homolog, congeners with fewer ortho-substituted chlorines have lower  $p_L^o$  and greater slopes. When these groupings are made (Fig. 1), regression of  $m_L$  values vs homolog within ortho-chlorine groups yield slopes of equation (1) that are functions of both homolog and ortho-chlorine number. These are the fitted  $m_L$  values in Table 2.

Foreman and Bidleman (1985) estimated vapor pressures at a single temperature (25°C) for 141 PCB congeners by correlating published retention indices at 200°C (OV-101 column) to  $p_L^o$  of the 30 PCBs in Bidleman (1984). Fischer *et al.* (1992) also estimated vapor pressures for 133 PCBs from GC retention data by a similar method. In their study, a SB-octyl 50 (methyl-50% *n*-octylpolysiloxane) column was used and reference vapor pressure data for 20 individual PCB congeners were taken from a review by Shiu and

Mackay (1986). Some of these vapor pressures may have been from Bidleman (1984), since these were listed in the review. Comparison of the Foreman and Bidleman (A) and Fischer *et al.* (B) vapor pressures showed very close agreement ( $r^2 = 0.993$ ), expressed by

$$\log p_L^o(A) = 0.992 \log p_L^o(B) - 0.0434. \quad (2)$$

Slight differences between the two data sets were accounted for by adjusting (B) values to (A) with equation (2) for congeners not in the original (A) set. Temperature coefficients for this larger set of PCB congeners (Table 3) were then estimated as follows: fitted  $m_L$  values were taken from Table 2 according to homolog and ortho-chlorine number, and  $b_L$  values were calculated from  $p_L^o$  at 25°C using equation (1). For the 32 congeners whose  $Q_1$  values were directly measured by capillary GC,  $m_L$  and  $b_L$  from Table 1 are repeated in Table 3.

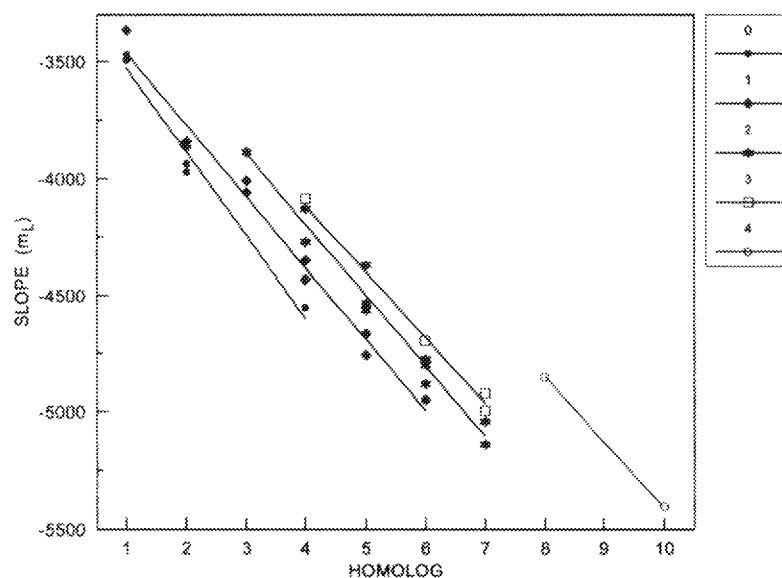


Fig. 1. Slope of equation (1) by homologs (1–10) and ortho-chlorine groups (0–4). Data from Table 1.

Table 2. Fitted  $m_L$  for different ortho-chlorine substitutions\*

Homolog	Number of ortho-chlorines				
	0	1	2	3	4
1	-3528	-3462	—	—	—
2	-3885	-3769	-3642	—	—
3	-4242	-4075	-3935	-3836	—
4	-4598	-4382	-4229	-4117	-3751
5	-4956	-4688	-4522	-4399	-4027
6	-5313	-4994	-4816	-4681	-4303
7	—	-5300	-5109	-4962	-4579
8	—	—	-5402	-5244	-4851
9	—	—	—	-5526	-5127
10	—	—	—	—	-5402

\* From Fig. 1.

Table 3. Parameters of equation (1) for calculation of vapor pressure (Pa) for PCBs

Congener	Total chlorines	Ortho-chlorines	$m_L$	$b_L$
1	1	1	-3366	11.57
2	1	0	-3476	11.65
3	1	0	-3488	11.67
4	2	2	-3642	11.73
5*	2	1	-3769	11.81
6	2	1	-3769	11.88
7	2	1	-3841	12.15
8	2	1	-3769	11.84
9	2	1	-3862	12.22
10	2	2	-3642	11.74
11	2	0	-3936	12.14
12	2	0	-3885	11.92
13	2	0	-3885	11.95
14	2	0	-3885	12.13
15	2	0	-3971	12.18
16	3	2	-3935	11.93
17	3	2	-3935	12.05
18	3	2	-3935	12.09
19	3	3	-3836	11.93
20	3	1	-4075	12.12
21*	3	1	-4075	12.11
22	3	1	-4075	12.08
23*	3	1	-4075	12.36
24*	3	2	-3935	12.02
25	3	1	-4075	12.24
26	3	1	-4075	12.28
27	3	2	-3935	11.97
28	3	1	-4075	12.20
29	3	1	-4007	12.09
30	3	2	-3886	12.02
31	3	1	-4058	12.15
32	3	2	-3935	11.93
33	3	1	-4075	12.09
34*	3	1	-4075	12.37
35	3	0	-4242	12.37
36*	3	0	-4242	12.48
37	3	0	-4242	12.33
39	3	0	-4242	12.53
40	4	2	-4271	12.32
41	4	2	-4229	12.22
42	4	2	-4229	12.25
43	4	2	-4229	12.40
44	4	2	-4229	12.29
45	4	3	-4117	12.16
46	4	3	-4117	12.08
47	4	2	-4229	12.37
48	4	2	-4229	12.37
49	4	2	-4229	12.41
51*	4	3	-4117	12.20
52	4	2	-4220	12.36
53	4	3	-4114	12.24
54	4	4	-3751	11.17
55	4	1	-4382	12.46
56	4	1	-4382	12.33
60	4	1	-4382	12.42
61†	4	1	-4382	12.78
63*	4	1	-4382	12.53
64*	4	2	-4229	12.30
65*	4	2	-4229	12.33
66	4	1	-4349	12.38
67*	4	1	-4382	12.52
69*	4	2	-4229	12.43
70	4	1	-4431	12.60
71	4	2	-4229	12.14
72	4	1	-4382	12.70
74	4	1	-4382	12.56
75	4	2	-4229	12.44
76	4	1	-4382	12.48
77	4	0	-4552	12.61

Table 3. (continued)

Congener	Total chlorines	Ortho-chlorines	$m_L$	$b_L$
78	4	0	-4598	12.92
79	4	0	-4598	12.95
80	4	0	-4598	13.16
81	4	0	-4598	12.88
82 <sup>+</sup>	5	2	-4522	12.63
83	5	2	-4522	12.60
84	5	3	-4399	12.32
85	5	2	-4522	12.54
86*	5	2	-4522	12.61
87	5	2	-4562	12.66
88*	5	3	-4399	12.53
90*	5	2	-4522	12.69
91	5	3	-4399	12.44
92	5	2	-4522	12.76
93*	5	3	-4399	12.57
95	5	3	-4399	12.48
97	5	2	-4522	12.56
98	5	3	-4399	12.54
99	5	2	-4533	12.68
101	5	2	-4514	12.67
102	5	3	-4399	12.48
103	5	3	-4399	12.70
105	5	1	-4758	12.90
106	5	1	-4688	12.86
107*	5	1	-4688	12.82
108	5	1	-4688	12.87
110	5	2	-4522	12.43
112*	5	2	-4522	12.65
113	5	2	-4522	12.63
114	5	1	-4688	12.82
115*	5	2	-4522	12.50
116*	5	2	-4522	12.53
117*	5	2	-4522	12.56
118	5	1	-4664	12.72
119*	5	2	-4522	12.61
120	5	1	-4688	13.02
121	5	2	-4522	12.85
122	5	1	-4688	12.72
123	5	1	-4688	12.84
124 <sup>+</sup>	5	1	-4688	12.62
125*	5	2	-4522	12.45
126	5	0	-4956	13.31
127	5	0	-4956	13.51
128	6	2	-4881	12.91
129*	6	2	-4816	12.80
130*	6	2	-4816	12.89
131	6	3	-4681	12.80
132	6	3	-4681	12.58
133	6	2	-4816	13.08
134	6	3	-4681	12.79
135	6	3	-4681	12.76
136	6	4	-4303	11.63
137*	6	2	-4816	12.61
138	6	2	-4800	12.81
139*	6	3	-4681	12.78
141*	6	2	-4816	12.94
143	6	3	-4681	12.65
144*	6	3	-4681	12.70
145*	6	4	-4303	11.90
146	6	2	-4816	13.04
148	6	3	-4681	12.98
149	6	3	-4689	12.78
151	6	3	-4681	12.95
153	6	2	-4775	12.85
154	6	3	-4681	12.94
155 <sup>+</sup>	6	4	-4303	12.02
156	6	1	-4949	12.94
157	6	1	-4994	13.05
158	6	2	-4816	12.94

Table 3. (continued)

Congener	Total chlorines	Ortho-chlorines	$m_L$	$b_L$
163	6	2	-4816	12.93
167	6	1	-4994	13.20
168	6	2	-4816	12.99
169*	6	0	-5313	13.64
170	7	2	-5139	13.17
171	7	3	-5008	13.07
172*	7	2	-5109	13.28
174	7	3	-4962	12.90
175*	7	3	-4962	13.22
176	7	4	-4579	12.07
177	7	3	-4962	13.04
178*	7	3	-4962	13.28
179	7	4	-4579	12.07
180	7	2	-5042	13.03
181	7	3	-4962	13.11
182	7	3	-4962	13.11
183	7	3	-4962	13.19
185	7	3	-4962	13.15
186	7	4	-4579	12.03
187	7	3	-4911	12.96
188	7	4	-4579	12.29
189	7	1	-5300	13.46
190	7	2	-5109	13.17
191*	7	2	-5109	13.15
192	7	2	-5109	13.38
193	7	2	-5109	13.27
194	8	2	-5402	13.43
195	8	3	-5244	13.24
196	8	3	-5244	13.37
197	8	4	-4851	12.52
198	8	3	-5244	13.42
199	8	3	-5244	13.36
200	8	4	-4851	12.24
201	8	4	-4851	12.51
202	8	4	-4851	12.99
203	8	3	-5244	13.39
204	8	4	-4851	12.46
205	8	2	-5402	13.51
206	9	3	-5526	13.57
207	9	4	-5127	12.70
208	9	4	-5127	12.68
209	10	4	-5402	13.27

\*Vapor pressures taken from Fischer *et al.*, 1992, and corrected to GC values.†Vapor pressures taken from Dunnivant *et al.*, 1992, and corrected to GC values.‡Vapor pressures taken from Murphy *et al.*, 1987, and corrected to GC values.

The accuracy of these results can be assessed relative to independent sets of vapor pressures from Murphy *et al.* (1987) and Dunnivant *et al.* (1992). The former were obtained by determining the equilibrium composition of the headspace air over water saturated with Aroclor fluids at 20°C, and yielded not only vapor pressures but also water solubilities and Henry's law constants. Their calculation of  $p_L^0$  was based on the assumption that Aroclor fluids behave ideally (follow Raoult's law). Dunnivant *et al.* (1992) used quantitative structure-property relationship (QSPR) models to calculate solid-phase water solubilities ( $S_g^0$ ) and Henry's law constants of PCBs at 25°C. Assuming that differences between solid- and liquid-phase heat capacities were negligible, we converted values of  $S_g^0$  to sub-cooled liquid solubilities ( $S_L^0$ ,  $\text{mol m}^{-3}$ ) using the relationship

$$\ln S_L^0/S_g^0 = (\Delta S_f/RT)(T_m - T) \quad (3)$$

where  $\Delta S_f$  is the entropy of fusion,  $T_m$  is the melting temperature and  $T$  is the ambient temperature (Kelvin). Experimental  $\Delta S_f$  were used when available (Miller *et al.*, 1984); otherwise  $\Delta S_f = 56.5 \text{ J deg}^{-1} \text{ mol}^{-1}$  was assumed (Hinckley *et al.*, 1990). The resulting  $S_L^0$  values were multiplied by the Henry's law constants ( $\text{Pa m}^3 \text{ mol}^{-1}$ ) to yield  $p_L^0$ .

Values of  $p_L^0$  based on GC measurements (from Table 3 at 20 or 25°C) were compared to those determined by headspace analysis (20°C, Murphy *et al.*, 1987) and QSPR models (25°C, Dunnivant *et al.*, 1992). The seven congeners used to calibrate the original GC method (Bidleman, 1984; Hinckley *et al.*, 1990) were omitted from this comparison. The mean vapor pressure ratio (GC/Murphy) for 58 con-

geners was  $1.55 \pm 0.60$  (Murphy) vs  $\log p_L^0$  (GC ratio (GC/Dunnivant)  $\pm 0.65$ . Regression of (GC) yielded  $r^2 = 0.98$ . vapor pressures depend on pressure standards used in literature vapor pressure known within a factor of 10. other data sets for PCBs inherent in assuming model calculations (Dunnivant) yield PCB vapor pressures the average, which is for organic compounds. To data set, some of Murphy were adjusted to the regression equations a

Figure 2 compares a (Murphy) methods with the same groups. In both cases congeners having greater "ortho-effect" is not significant pressure technique.

The accuracy of vapor ( $m_L$  values in equation  $Q_2$ , the heat of vaporization used in the GC method DDT (Hinckley *et al.*, values were determined

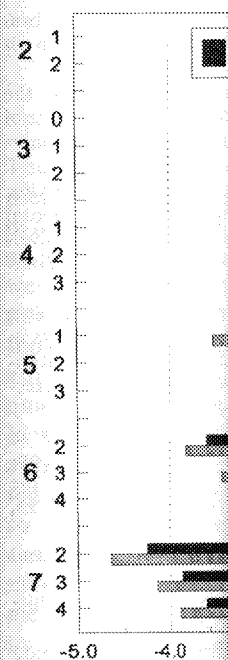


Fig. 2. Comparison of vapor pressures determined by gas chromatography (GC) and headspace analysis (Murphy *et al.*, 1987). The small ones to the



gers was  $1.55 \pm 0.60$  (s.d.). Regression of  $\log p_L^*$  (Murphy) vs  $\log p_L^*$  (GC) yielded  $r^2 = 0.981$ . The mean ratio (GC/Dunnivant) for 23 congeners was  $1.40 \pm 0.65$ . Regression of  $\log p_L^*$  (Dunnivant) vs  $\log p_L^*$  (GC) yielded  $r^2 = 0.981$ . The accuracy of GC-based vapor pressures depends on the accuracy of the vapor pressure standards used for calibration. Typically literature vapor pressures of these standards are known within a factor of two (Bidleman, 1984). The other data sets for PCBs also involve uncertainties inherent in assuming ideal behavior (Murphy) or model calculations (Dunnivant). All three methods yield PCB vapor pressures which agree within 50% on the average, which is very good for semivolatile organic compounds. To make a larger, more consistent data set, some of Murphy's and Dunnivant's  $p_L^*$  values were adjusted to the GC scale by their respective regression equations and added to Table 3.

Figure 2 compares average  $p_L^*$  by GC and headspace (Murphy) methods within homolog and ortho-chlorine groups. In both cases, higher  $p_L^*$  were found for congeners having greater numbers of ortho-chlorines. This result is important because it indicates that the "ortho-effect" is not simply an artifact of the GC vapor pressure technique.

The accuracy of vapor pressure temperature slopes ( $m$  values in equation (1)) depends on the reliability of  $Q_v$ , the heat of vaporization for standard substances used in the GC method, in this case eicosane and *p*, *p'*-DDT (Hinckley *et al.*, 1990). In the latter reference,  $m$  values were determined by GC for four PCBs, six

organochlorine pesticides and seven polycyclic aromatic hydrocarbons. As percentages of literature values, GC results ranged from -16 to +18%, with a mean of +3%. The  $m$  values in Tables 1 and 3 should have a similar degree of reliability.

### 3. PREDICTION OF THE AEROSOL-BOUND FRACTION OF PCBs

Estimating the fraction of a semivolatile organic compound adsorbed to particles ( $\Phi$ ) can be done using the Junge-Pankow model (Pankow, 1987)

$$\Phi = c\Theta/(p_L^* + c\Theta) \quad (4)$$

where  $\Theta$  is the particle surface area available for adsorption ( $\text{cm}^2 \text{ cm}^{-3} \text{ air}$ ) and  $c = 17.2 \text{ Pa-cm}$ . Values of  $\Theta$  have been suggested (Bidleman, 1988), based on Whitby's (1978) size distribution of accumulation mode aerosols: urban air =  $1.1 \times 10^{-5}$ , average continental background air =  $1.5 \times 10^{-6}$ , clean continental background air =  $4.2 \times 10^{-7}$ .

Particulate percentages at specified temperatures were obtained by first using  $m$  and  $b_L$  values from Table 3 to calculate  $p_L^*$ , then using the Junge-Pankow equation. Figure 3 shows the results of this model for urban air ( $\Theta = 1.1 \times 10^{-5}$ ; Bidleman, 1988) at 10 and 25°C for PCBs by homolog and ortho-chlorine substitution. At both temperatures, PCBs which are less ortho-substituted are preferentially sorbed to particles. The degree of adsorption within a homolog

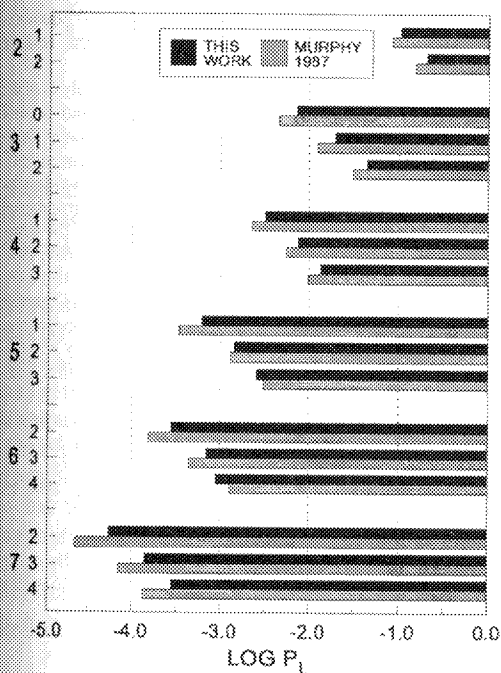


Fig. 2. Comparison of average vapor pressures ( $\log p_L^*$ ) by gas chromatography (GC) and headspace analysis (Murphy *et al.*, 1987). Large numbers refer to homolog, small ones to the number of ortho-chlorines.

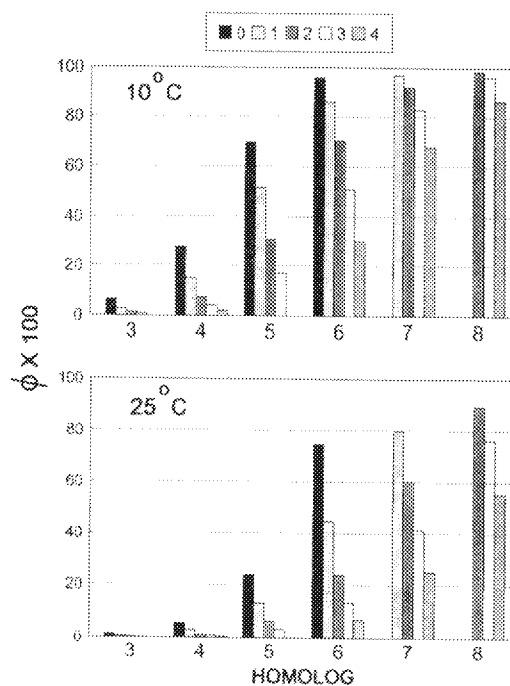


Fig. 3. Percent particulate PCBs ( $\Phi \times 100$ ) in urban air at 10 and 25°C by homolog (number) and ortho-chlorine (shade).





follows the order (number of ortho-chlorines):  $0 > 1 > 2 > 3 > 4$ . Average  $\Phi$  at  $10^\circ\text{C}$  for the non-orthotetrachlorobiphenyls and pentachlorobiphenyls are 3.8- and 2.3-times those for the di-ortho congeners. Smaller but substantial differences can be seen between mono- and diorthotetrachlorobiphenyls (factor of 2.0) and mono- and diorthopentachlorobiphenyls (factor of 1.7).

#### 4. CONCLUSIONS

The average agreement between GC and other methods for  $p_L^*$  was better than a factor of two, which is very good for semivolatile organic compounds. We thus conclude that Table 3 gives a set of consistent and accurate  $p_L^*$  values as functions of temperature and ortho-chlorine substitution that can be used as a basis for understanding the gas/particle partitioning of PCBs.

High volume sampling of urban air has yielded apparent partition coefficients of PCB congeners between the gas and aerosol phases that were closely correlated with their  $p_L^*$  values (Cotham, 1990; Foreman and Bidleman, 1990). Duinker and Bouchertall (1989) found that PCB profiles in rain more closely matched the atmospheric particulate fraction than the gas-phase. Although the particle/gas distribution of coplanar PCBs in air has not yet been determined experimentally, the expectation is for them to exhibit greater attachment to aerosols relative to other congeners of the same homolog, and to be selectively deposited.

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## A CO FOR THE PRECIP

Atmospheric Science

**Abstract**—The Regional puff model that simulates the eastern United States RELMAP overestimates grid-scale variability in precipitation observations by unacceptable levels. The effects of original and updated length scales of the RELMAP by as much as 400% (Distribution (CED)) and accurate estimates of intensively applied on version of RELMAP estimates by 6–12%. CED analysis offers to otherwise preclude the

**Key word index:** Wet Regional Air Pollution

## 1. INTRO

The removal of atmospheric precipitation processes is known of increased acidity in rain in the eastern U.S.A. and southern wet or dry removal, atmospheric to be a major contributor to those same areas. Because atmospheric sulfur in these quality, the U.S. EPA has set of various numerical models atmospheric sulfur cycle, regulatory purposes often use so that they may be operated computing systems. Obviously more opportunity for sub-meteorological variables, in its effect on wet deposition

\* On assignment to the Atmospheric Assessment Laboratory, U.S. Agency.